

Dynamic mean-field models from a nonequilibrium thermodynamics perspective

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Complicated dynamic models are often approximated by introducing mean-field approximations and closures. The focus here is on examining such mean-field models using nonequilibrium thermodynamics. Two illustrative examples are studied in terms of the double-generator general equation for the nonequilibrium reversible-irreversible coupling (GENERIC) framework. First, it is shown that a model for the coil-stretch transition of long chains in strong elongation flows as proposed by de Gennes is thermodynamically admissible. In the second example, we study a Gaussian approximation, which is used to simplify the effect of hydrodynamic interactions in polymer solutions. This approximation, which is known to be in conflict with the fluctuation-dissipation theorem, is identified as defective directly when formulated in the thermodynamic formalism.

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I. INTRODUCTION

Models in polymer kinetic theory are often based on the notion of bead positions or connector vectors. This amounts to a convenient way to study also complicated effects, such as the finite extensibility of the chains and many-body hydrodynamic interaction. However, such models derived or postulated in terms of the distribution function of bead positions or connector vectors are then hard to analyze analytically, and great efforts are required in order to extract useful information. Due to this, simplifications are made. Either the method of reduction is employed (for a recent review, see Ref. [1]) or part of the complicated dependence on the bead configuration is replaced by a dependence on moments of the distribution function, for example. In practice, these two different ways to make the models more tractable are often applied simultaneously. In this paper, we are concerned with the second of the strategies just mentioned, in the following referred to as mean-field approximations.

The significance of mean-field approximations goes beyond the mathematical simplification of complicated equations, as they are often also physically well motivated and allow one to account for collective effects in models with few degrees of freedom. Nonetheless, it is not *a priori* clear whether such approximations, i.e., alterations of the functional form of the dynamic equations, still agree with the laws of thermodynamics. Our goal is, by studying examples specific to the practice of modeling in complex fluids, to elaborate on how nonequilibrium thermodynamic techniques shed a different light on mean-field approximations.

The manuscript is organized as follows. In Sec. II, we briefly describe the double-generator general equation for the nonequilibrium reversible-irreversible coupling (GENERIC) framework of nonequilibrium thermodynamics, which shall be employed to analyze the mean-field models. Section III

examines the thermodynamic compatibility of de Gennes's model for the coil-stretch transition, whereas in Sec. IV a so-called Gaussian approximation for dilute polymer solutions with hydrodynamic interaction is reviewed and examined. Finally, the results are discussed in Sec. V.

II. METHOD

Nonequilibrium thermodynamics is ubiquitous when modeling dynamic, out-of-equilibrium systems, and is represented in different formalisms. The framework outlined by de Groot and Mazur in Ref. [2] defines the state of the art of linear irreversible thermodynamics. Based upon the introduction of dissipative brackets [3–6], the single-generator bracket formalism [7], and subsequently, the double-generator GENERIC framework emerged [8,9], encompassing also nonlinear phenomena. The latter two additionally require the Jacobi identity for the reversible dynamics. The relation of the GENERIC framework to other formalisms, including those mentioned above, has been established in Refs. [9–12]. Except if specifically interested in time-structure invariance, i.e., in the Jacobi identity, or nonlinear effects, either formalism may equally be employed. We here choose the GENERIC for the further discussion of the mean-field models.

The time evolution equations for the variables x , which describe the closed system to the desired detail and may have both discrete and continuous indices, are given in the GENERIC framework by

$$\frac{dx}{dt} = L \frac{\delta E}{\delta x} + M \frac{\delta S}{\delta x}, \quad (1)$$

where the two generators E and S are the total energy and entropy functionals in terms of the state variables x and L and M are certain operators. The matrix multiplications do not only imply summations over discrete indices but may also include integration over continuous variables, and $\delta/\delta x$ typically implies functional rather than partial derivatives (for more details, see Refs. [8,9]). The evolution equation (1) is supplemented by the degeneracy requirements

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$$L \frac{\delta S}{\delta x} = 0, \quad (2)$$

$$M \frac{\delta E}{\delta x} = 0, \quad (3)$$

stating that the functional forms of S and L are constrained such that the entropy is not affected by the reversible dynamics, and that the total energy is not altered by the irreversible dynamics, respectively. Finally, the GENERIC structure requires that L must be antisymmetric and fulfill the Jacobi identity, whereas M needs to be positive semidefinite and Onsager-Casimir symmetric. As a consequence of all these conditions, one may easily show that Eq. (1) implies both the conservation of total energy as well as a non-negative entropy production. The two contributions to the time evolution of x generated by the total energy E and the entropy S in Eq. (1) are called the reversible and irreversible contributions, respectively.

III. EXAMPLE 1: THERMODYNAMIC ADMISSIBILITY OF A MODEL FOR THE COIL-STRETCH TRANSITION

A. Problem statement

The shape of a polymer is distorted when it is exposed to an inhomogeneous flow field, in particular, if the deformation rate is large compared to the characteristic molecular relaxation time. The following two effects need to be considered in the modeling of chain distortion. First, the extension of the chain tends to saturate, which in a bead-spring model is described by a diverging interaction force at a critical bead separation, the so-called finitely extensible nonlinear elastic (FENE) forces such as the inverse Langevin force law or the Warner force law (see, e.g., Refs. [13–15]). Second, the hydrodynamic interactions between monomers decrease when the polymer is stretched, as almost all monomers are then exposed to the flow field (see Ref. [16] for more details).

In order to set up a closed dynamic equation for the second moment of the chain end-to-end vector, de Gennes [16] and Fuller and Leal [17] have used the ‘‘Peterlin’’ approximation of the FENE interaction and a ‘‘mean-field’’ diffusion coefficient, which results in the following evolution equation for the second moment $\Theta = \langle \mathbf{Q}\mathbf{Q} \rangle$ in homogeneous flow conditions, with $\kappa_{ij} = \partial_{r_j} v_i$:

$$\partial_t \Theta_{ij} = \kappa_{im} \Theta_{jm} + \Theta_{im} \kappa_{jm} - 2D(\Theta) \left(\frac{H(\Theta)}{k_B T} \Theta_{ij} - \delta_{ij} \right). \quad (4)$$

The configuration dependent diffusion coefficient D and the FENE-P spring constant H , here assumed to be of the Warner form, are

$$D(\Theta) = \frac{R_0^2}{3\tau(\Theta)} = \frac{R_0^2}{3\tau_R} \left(1 + \frac{u}{t(\Theta)} \right), \quad (5)$$

$$H(\Theta) = \frac{H_0}{1 - t(\Theta)^2}, \quad (6)$$

with

$$t(\Theta) := \frac{\sqrt{\text{tr}(\Theta)}}{L}, \quad (7)$$

a constant relaxation time τ_R , H_0 linear in T , and the parameter u of order unity [16]. L denotes the maximum possible spring extension. In the limit $L \rightarrow \infty$, we obtain a Hookean spring-force law with spring constant H_0 . The quantity $t(\Theta)$ measures the actual end-to-end distance in units of the maximal extension. In the steady state of planar elongation flows,

$$\kappa = \begin{pmatrix} \dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon} & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (8)$$

all of these works just mentioned find S -shaped curves for the mean-square end-to-end distance as a function of deformation rate. De Gennes [16] discusses these curves in terms of coil \rightleftharpoons stretch transitions, and Fuller and Leal state that the hysteresis effects associated with the S -shaped curves have important implications for a better understanding of drag reduction. It has been argued by Fan *et al.* [18] that the origin of such S -shaped curves must lie in the mean-field approximations introduced into the diffusion coefficient $D(\Theta)$ and into the spring coefficient $H(\Theta)$, since Brownian dynamics simulations of the FENE model, i.e., without any mean-field approximations, with a \mathbf{Q} -dependent diffusion coefficient do not show such S -shaped curves. Apart from their fundamentally different behavior in flow, the two models also differ in their motivation. In particular, de Gennes’s expression for the diffusion coefficient (5) is motivated by considering a long, many-bead chain, for which the effective hydrodynamic interactions change strongly in going from coiled to stretched conformations, whereas the model studied by Fan *et al.* uses the concept of dumbbells. One should thus not consider one model being a subcase of the other, but rather see them as just two different models. Then, the question of thermodynamic admissibility of the two models arises individually. The full FENE model studied by Fan *et al.* can be formulated within the GENERIC framework in a straightforward manner considering the corresponding example in Ref. [9]. We here intend to show whether the second-rank tensor model proposed by de Gennes (4) *per se* can be captured in the GENERIC formalism.

We mention that de Gennes’s model is a nice illustration of the observation that a mean-field model should not necessarily be considered as a mean-field approximation to some other model, even if there is a close formal relationship. Another important illustration of this situation is the use of the mean-field models of dilute polymer solutions in the investigation of wall turbulent flow [19]. Experimental observations can be reproduced semiquantitatively by choosing relaxation times that are unrealistically large for single-polymer molecules. Therefore, these large relaxation times

should be considered as a mean-field description of collective phenomena which are plausible because the solutions are typically close to the overlap concentration at equilibrium, and the polymer molecules become significantly stretched by the flow so that interactions are expected to occur.

B. GENERIC formulation of de Gennes's model

The variables to describe the system shall be given by the mass density $\rho(\mathbf{r})$ of the solution, the momentum density $\mathbf{u}(\mathbf{r})$ of the solution, the internal energy density $\epsilon(\mathbf{r})$ of the solvent, and the second moment $\Theta(\mathbf{r})$ of the configurational distribution function, i.e., by the set

$$\mathbf{x} = \{\rho(\mathbf{r}), \mathbf{u}(\mathbf{r}), \epsilon(\mathbf{r}), \Theta(\mathbf{r})\}. \quad (9)$$

Since the bead interaction is purely of entropic origin, the total energy does not depend on the second moment and is given by

$$E = \int \left(\frac{\mathbf{u}^2}{2\rho} + \epsilon \right) d^3r. \quad (10)$$

As far as the entropy functional S is concerned, we start at writing down the configurational entropy S^{conf} for the FENE model in the distribution function formulation. Let $\psi(\mathbf{r}, \mathbf{Q})$ denote the number of dumbbells with bead connector vector \mathbf{Q} at (fixed) position \mathbf{r} , and normalization

$$\int \psi(\mathbf{r}, \mathbf{Q}) d^3Q = n_p \quad (11)$$

at polymer concentration n_p . The configurational entropy is then [9]

$$S^{\text{conf}}(\psi) = -k_B \int \psi \left[\ln \psi + \frac{V^{\text{pot}}(Q^2)}{k_B T} \right] d^3Q d^3r \quad (12)$$

$$\equiv -n_p k_B \int \left\langle \ln \psi + \frac{V^{\text{pot}}(Q^2)}{k_B T} \right\rangle_{\psi} d^3r, \quad (13)$$

with

$$V^{\text{pot}}(Q^2) = V^{\text{FENE}}(Q^2) = -\frac{H_0 L^2}{2} \ln \left(1 - \frac{Q^2}{L^2} \right), \quad (14)$$

where $\langle \dots \rangle_{\psi}$ denotes the average with respect to the distribution of the bead connector vector \mathbf{Q} .

Since we aim at capturing de Gennes's closed second-moment equation (4), we consistently assume the distribution function to be Gaussian in the first term of S^{conf} and use only the resummation of the lowest-order cumulants of the cumulant expansion, i.e., the first term on the right-hand side of

$$\langle f(x) \rangle = f(\langle x \rangle) + \sum_{m=1}^{\infty} \frac{1}{m!} \left(\frac{\langle x^2 \rangle_c}{2} \right)^m \frac{d^2m}{dx^{2m}} f(x) \Big|_{x=\langle x \rangle} + \dots \quad (15)$$

with $x = Q^2/L^2$, for the V^{FENE} contribution. Further terms of this expansion can be used to improve the FENE-P approximation, see Ref. [1]. Expressing the result in terms of the second moment, the total entropy reads

$$S = \int s^{\text{tot}} d^3r = \int s(\rho, \epsilon) d^3r + S^{\text{conf}} \quad (16)$$

$$= \int \left\{ s(\rho, \epsilon) + \frac{n_p k_B}{2} \left(\ln \left[\det \frac{H_0}{k_B T} \Theta \right] + \frac{H_0 L^2}{k_B T} \times \ln \left[1 - \frac{\text{tr}(\Theta)}{L^2} \right] \right) \right\} d^3r, \quad (17)$$

up to additive constants for constant polymer density n_p . Realizing that the ratio H_0/T does not depend on any of the fundamental variables, the functional derivatives of the generating functionals become

$$\frac{\delta E}{\delta \mathbf{x}} = \begin{pmatrix} -\frac{1}{2} \mathbf{v}^2 \\ \mathbf{v} \\ 1 \\ \mathbf{0} \end{pmatrix}, \quad \frac{\delta S}{\delta \mathbf{x}} = \begin{pmatrix} -\frac{\mu}{T} \\ 0 \\ \frac{1}{T} \\ \frac{n_p k_B}{2} \left(\Theta^{-1} - \frac{H(\Theta)}{k_B T} \mathbf{1} \right) \end{pmatrix}. \quad (18)$$

As elaborated in Ref. [20], the reversible dynamics for the set of variables (9) is given by the Poisson operator

$$L = - \begin{pmatrix} 0 & \nabla_k \rho & 0 & 0 \\ \rho \nabla_i & \nabla_k u_i + u_k \nabla_i & L_{u_i \epsilon} & L_{u_i \Theta_{kl}} \\ 0 & L_{\epsilon u_k} & 0 & 0 \\ 0 & L_{\Theta_{ij} u_k} & 0 & 0 \end{pmatrix}, \quad (19)$$

with

$$L_{u_i \epsilon} = \nabla_i p + \epsilon \nabla_i + \nabla_k \Pi_{ki}, \quad (20)$$

$$L_{\epsilon u_k} = p \nabla_k + \nabla_k \epsilon + \Pi_{ki} \nabla_i, \quad (21)$$

$$L_{u_i \Theta_{kl}} = -(\nabla_i \Theta_{kl}) - \nabla_m \Theta_{mk} \delta_{il} - \nabla_m \Theta_{ml} \delta_{ik}, \quad (22)$$

$$L_{\Theta_{ij} u_k} = (\nabla_k \Theta_{ij}) - \Theta_{im} \nabla_m \delta_{jk} - \Theta_{jm} \nabla_m \delta_{ik}. \quad (23)$$

The pressure p is

$$p = -\epsilon + \left(\frac{\partial S^{\text{tot}}}{\partial \epsilon} \right)^{-1} \left(s^{\text{tot}} - \rho \frac{\partial S^{\text{tot}}}{\partial \rho} \right) \quad (24)$$

and the osmotic pressure tensor Π_{ij} , generally given by

$$\Pi_{ij} = 2T \Theta_{ki} \frac{\partial S^{\text{tot}}}{\partial \Theta_{jk}}, \quad (25)$$

in the present case reduces to

$$\mathbf{\Pi}(\mathbf{r}) = n_p [k_B T(\mathbf{r}) \mathbf{1} - H(\mathbf{\Theta}(\mathbf{r})) \mathbf{\Theta}(\mathbf{r})], \quad (26)$$

with the configuration dependent spring constant (6). It is shown in Ref. [20] that the Poisson operator given by Eqs. (19)–(25) fulfills all the GENERIC requirements, i.e., it is antisymmetric, and fulfills both the degeneracy requirement as well as the Jacobi identity.

We now proceed to the formulation of the irreversible contributions. Inspection of Eqs. (4) and (18) shows that a natural choice for the M matrix is

$$M = \begin{pmatrix} \dots & \dots & \dots & 0 \\ \dots & \dots & \dots & 0 \\ \dots & \dots & \dots & 0 \\ 0 & 0 & 0 & \frac{1}{n_p} T S_{ijkl} \end{pmatrix}, \quad (27)$$

where the dots stand for the usual entries of classical hydrodynamics corresponding to viscous stresses and heat conduction (see, e.g., Ref. [9]) and the fourth-rank tensor S_{ijkl} is given by

$$S_{ijkl} = \frac{D(\mathbf{\Theta})}{k_B T} (\delta_{ik} \Theta_{jl} + \delta_{jk} \Theta_{il} + \delta_{il} \Theta_{jk} + \delta_{jl} \Theta_{ik}). \quad (28)$$

The resulting M matrix is symmetric and inherits the positive semidefiniteness from the second moment $\mathbf{\Theta}$ and from the diffusion coefficient $D(\mathbf{\Theta})$, thus fulfilling all requirements of the GENERIC [20]. Apart from the configuration dependence of the diffusion coefficient $D(\mathbf{\Theta})$ according to Eq. (5), we mention that expression (28) is identical to the relaxation tensor of the Maxwell and Oldroyd B models.

In summary, we find that the final evolution equations deduced from the building blocks E [Eq. (10)], S [Eq. (17)], L [Eqs. (19)–(26)], and M [Eqs. (27) and (28)] are the generalization of de Gennes's second-moment equation (4) to arbitrary flows and nonisothermal conditions. Hence, de Gennes's model for the second moment is *per se* a thermodynamically admissible model, and conclusively, also the associated coil \rightleftharpoons stretch transitions and hysteresis effects. One should notice that the characteristics specific to de Gennes's model enter into the expressions for the spring-force law (6), i.e., entropy (17), and into the conformation-dependent diffusion coefficient (5) in Eq. (28). Whereas the former is based on the cumulant expansion, the form of the latter relies on physical intuition. Apart from positivity, the diffusion coefficient is not otherwise restricted from within the framework, and needs to be elaborated on separate grounds, as illustrated, e.g., by de Gennes [16] for the model discussed above.

IV. EXAMPLE 2: LINEAR STOCHASTIC PROCESS BEHIND THE GAUSSIAN APPROXIMATION

A. Problem statement

In this second example, we consider a dilute solution of hydrodynamically interacting dumbbells, described by the diffusion equation (see also, e.g., Refs. [9,13,21])

$$\begin{aligned} \partial_t \psi = & -\nabla_{r_i} (\psi v_i) - \nabla_{Q_i} [(\nabla_{r_j} v_i) Q_j \psi - 2R_{ij} (\nabla_{Q_j} V^S) \psi] \\ & + 2k_B T \nabla_{Q_i} R_{ij} \nabla_{Q_j} \psi. \end{aligned} \quad (29)$$

for the distribution function $\psi(\mathbf{r}, \mathbf{Q})$ with an entropic Hookean spring potential

$$V^S = \frac{H}{2} Q^2, \quad (30)$$

with $H \propto T$ [9]. In Eq. (29), the configuration dependent diffusion matrix \mathbf{R} is given by

$$R_{ij} = \frac{1}{\zeta} (\delta_{ij} - \zeta \Omega_{ij}), \quad (31)$$

where ζ is the friction coefficient of a single bead, and where Ω_{ij} is the \mathbf{Q} -dependent hydrodynamic interaction tensor of the form (for more details, see, e.g., Refs. [13,21])

$$\Omega_{ij} = f(Q) \delta_{ij} + g(Q) Q_i Q_j, \quad (32)$$

with the incompressibility condition

$$\partial_{Q_i} \Omega_{ij} = 0. \quad (33)$$

Deducing the first- and second-moment equations from Eq. (29), one finds, on one hand, $\alpha_i \equiv \langle Q_i \rangle = 0$, and on the other hand, that the equation for the second moment $\Theta_{ij} \equiv \langle Q_i Q_j \rangle$ is not closed but rather includes higher moments of the distribution functions due to the \mathbf{Q} dependence of the matrix R_{ij} . There are different ways to close the evolution equation for the second moment. First, one may replace the matrix R_{ij} in the diffusion equation (29) by its equilibrium average $\langle R_{ij} \rangle_{\psi_{\text{eq}}}$, which is the so-called preaveraging method [22], or, second, by its average $\langle R_{ij} \rangle_{\psi(t)}$ with respect to the actual distribution function, which is the so-called self-consistent averaging method [23]. In both methods, the resulting distribution function is Gaussian, since the diffusion equation has a drift term linear in \mathbf{Q} and a constant diffusion matrix. A further method is the so-called Gaussian approximation [24,25]. There, one derives the second-moment equation from Eq. (29) and assumes the distribution function to be Gaussian in order to evaluate all averages occurring. Doing so, the second-moment equation is closed. It has been shown that the shear rate dependent viscosity and the normal stress coefficients determined from the Gaussian approximation are in significantly better agreement with Brownian dynamics simulations of the unapproximated model than the other two approximations (see, e.g., p. 201 in Ref. [21]). Using

$$\psi^{\text{Gaussian}}(\mathbf{r}, \mathbf{Q}) = \frac{n_p}{\sqrt{(2\pi)^3 \det(\Theta(\mathbf{r}))}} \exp\left[-\frac{1}{2} \mathbf{Q} \cdot \Theta^{-1}(\mathbf{r}) \cdot \mathbf{Q}\right], \quad (34)$$

the closed second-moment equation, at constant polymer density n_p , becomes

$$\partial_t \Theta_{ij} = -v_m \nabla_{r_m} \Theta_{ij} + \kappa_{im} \Theta_{jm} + \Theta_{im} \kappa_{jm} + S_{ijkl} \left(\frac{k_B T}{2} \Theta_{kl}^{-1} - \frac{H}{2} \delta_{kl} \right) \quad (35)$$

with the transpose of the velocity gradient $\kappa_{ij} = \langle \nabla_j v_i \rangle$ and the fourth-rank tensor S_{ijkl} given by

$$S_{ijkl} = 2[\langle Q_i \hat{R}_{jk} Q_l \rangle + \langle Q_j \hat{R}_{ik} Q_l \rangle + \langle Q_i \hat{R}_{jl} Q_k \rangle + \langle Q_j \hat{R}_{il} Q_k \rangle] \quad (36)$$

and

$$\hat{\mathbf{R}} = \begin{cases} \langle \mathbf{R} \rangle_{\psi_{\text{eq}}} & \text{preaveraging} \\ \langle \mathbf{R} \rangle_{\psi(t)} & \text{self-consistent averaging} \\ \mathbf{R} & \text{Gaussian approximation.} \end{cases} \quad (37)$$

It is evident from Eqs. (36) and (37) that only the Gaussian approximation accounts for fluctuations in the hydrodynamic interaction tensor, whereas the others do not by construction.

From the above second-moment equation (35), the shear viscosity, in particular, also at zero-shear rate, can be computed since the shear stress is directly related to the second moment through $\tau_{xy} = n_p H \Theta_{xy}$. On the other hand, the zero-shear rate viscosity may also be computed in terms of equilibrium time-correlation functions using the fluctuation-dissipation theorem of the first kind [26], i.e., the Green-Kubo relation. Calculation of the latter requires the transition probabilities of the stochastic process. In the absence of mean-field contributions, the diffusion equation with appropriate initial condition, then also known as the Fokker-Planck equation, can be used to determine the transition probabilities of the Markov process [21,27]. However, special care is required in the presence of mean-field approximations, which introduce nonlinearities in terms of the distribution function into the diffusion equation. In Ref. [28], it has been shown that processes described by nonlinear diffusion equations lose the Markov property in transient situations, so that the diffusion equation cannot be used to calculate the transition probabilities in transient situations. In the context of the Green-Kubo relation here, the transition probabilities under stationary conditions only are needed, i.e., at equilibrium, where the processes are still Markovian. Nevertheless, one should bear in mind that by introducing mean-field approximations into the diffusion equation, as is done here, in general also non-Markov effects come into play.

In order to write the diffusion equations corresponding to the three approximations, one notices that in each case the drift term must be linear and the diffusion tensor constant in \mathbf{Q} [21,27], since the distribution functions are Gaussian.

Whereas the diffusion equation for the preaveraging and the self-consistent approximation, respectively, is obtained naturally by replacing the matrix \mathbf{R} in Eq. (29) with the according average, a diffusion equation corresponding to the Gaussian approximation needs to be constructed in a less straightforward way. It can be shown that

$$\partial_t \psi = -\nabla_{r_i} (\psi v_i) - \nabla_{Q_i} \kappa_{ij} Q_j \psi + \nabla_{Q_i} 2A_{ij} H Q_j \psi + 2k_B T \nabla_{Q_i} D_{ij} \nabla_{Q_j} \psi \quad (38)$$

with

$$A_{ij} = \langle R_{ij} \rangle_{\psi(t)} + \langle (\partial_{Q_j} R_{ik}) Q_k \rangle_{\psi(t)} + k_B T G_{ij}, \quad (39)$$

$$D_{ij} = \langle R_{ij} \rangle_{\psi(t)} + \frac{H}{2} (G_{ik} \Theta_{kj} + \Theta_{ik} G_{jk}) \quad (40)$$

results in the second-moment equation for the Gaussian approximation, after applying Wick's theorem to S_{ijkl} and assuming constant polymer density n_p . Note that for the preaveraging approximation $A_{ij} = D_{ij} = \langle R \rangle_{\psi_{\text{eq}}}$, whereas in the self-consistent approximation $A_{ij} = D_{ij} = \langle R \rangle_{\psi(t)}$. For the Gaussian approximation, it can be shown that the moment equations derived from Eq. (38) are invariant with respect to the inclusion of an arbitrary \mathbf{Q} -independent matrix G_{ij} according to Eqs. (39) and (40), where the only constraint on G_{ij} is the positivity of the diffusion matrix. In the following, we hence refer to Eqs. (39) and (40) for a specific choice of G_{ij} as a "gauge." The gauge with $G_{ij} = 0$ has been considered in Ref. [21]. However, expressions (39) and (40) with $G_{ij} = 0$ are then in conflict with the Green-Kubo relation for the zero-shear rate viscosity η_0 . In particular, the value obtained from the linear response of the second-moment equation to shear flow with shear rate $\dot{\gamma}$,

$$\eta_0^{\text{LR}} = \lim_{\dot{\gamma} \rightarrow 0} \frac{\tau_{xy}}{\dot{\gamma}} = \lim_{\dot{\gamma} \rightarrow 0} \frac{n_p H \Theta_{xy}}{\dot{\gamma}}, \quad (41)$$

does not correspond to the value obtained from evaluating the Green-Kubo relation,

$$\begin{aligned} \eta_0^{\text{GK}} &= \frac{1}{n_p k_B T} \int_0^\infty \langle \tau_{xy}(t) \tau_{xy}(0) \rangle_{\text{eq}} dt \\ &= \frac{n_p H^2}{k_B T} \int_0^\infty \langle Q_x(t) Q_y(t) Q_x(0) Q_y(0) \rangle_{\text{eq}} dt. \end{aligned} \quad (42)$$

One finds

$$\frac{\eta_0^{\text{GK}}}{\eta_0^{\text{LR}}} = \frac{1 - \frac{7}{10} \sqrt{2} h^*}{1 - \sqrt{2} h^*} \neq 1, \quad (43)$$

where the hydrodynamic interaction parameter h^* is defined as

$$h^* = \frac{\zeta}{6\pi\eta_s} \sqrt{\frac{H}{\pi k_B T}} \quad (44)$$

with η_s the solvent viscosity. For Ω_{ij} , the Oseen-Burgers tensor (see, e.g., Refs. [13,21]) has been used. Thus, according to Eq. (43), there is an inherent problem with the diffusion equation (38) when using expressions (39) and (40) with $G_{ij}=0$.

As discussed above, the purpose of writing the diffusion equation is to compute transition probabilities of the Markov process \mathbf{Q} [21,27] in the stationary equilibrium situation, which are needed for evaluation of the Green-Kubo relation. However, the construction of the diffusion equation with the second-moment equation (35) seems problematic for the Gaussian approximation, at least if $G_{ij}=0$. The one-time-quantity $\langle \tau_{xy}(t \rightarrow \infty) \rangle$ (i.e., η_0^{LR}) being gauge invariant, the question is to find a gauge in which the two-time-quantity $\langle \tau_{xy}(t) \tau_{xy}(0) \rangle_{\text{eq}}$ (i.e., η_0^{GK}) is tuned so as to match the Green-Kubo relation. In the following, we aspire to formulate a diffusion equation for the Gaussian approximation by using the GENERIC framework of nonequilibrium thermodynamics. Doing so, we focus on how this procedure guides us to a specific gauge G_{ij} , which does not conflict with the Green-Kubo relation.

B. GENERIC distribution function formulation

For formulating a diffusion equation in a closed system in terms of the GENERIC framework, we choose the set of variables (9), but replace the second moment by the distribution function $\psi(\mathbf{r}, \mathbf{Q})$ normalized as in Eq. (11), i.e.,

$$\mathbf{x} = \{ \rho(\mathbf{r}), \mathbf{u}(\mathbf{r}), \epsilon(\mathbf{r}), \psi(\mathbf{r}, \mathbf{Q}) \}. \quad (45)$$

As generating functionals, the total energy E is again given by Eq. (10), whereas the entropy S takes form (16) with the configurational contribution (12) using the Hookean force law (30). Their functional derivatives are thus given by the left part of Eq. (18) and

$$\frac{\delta S}{\delta \mathbf{x}} = \begin{pmatrix} -\frac{\mu}{T} \\ 0 \\ 1 \\ \frac{1}{T} \\ -k_B(\ln \psi + 1) - \frac{V^{(S)}}{T} \end{pmatrix}. \quad (46)$$

It has been discussed above that the Gaussian approximation is nontrivial only due to the \mathbf{Q} dependence of the friction matrix R_{ij} , i.e., it affects only the irreversible contributions. Hence, for the reversible dynamics we may use the Poisson operator L for unapproximated models including the distribution function as elaborated previously [9]. Only the elements L_{24} and L_{42} change in comparison to the Θ formulation [Eqs. (19)–(23)]:

$$L_{u_i \Theta_{kl}} \rightarrow L_{u_i \psi} = \psi(\mathbf{r}, \mathbf{Q}') \nabla_{r_i} - \nabla_{r_m} \psi(\mathbf{r}, \mathbf{Q}') Q'_m \nabla_{Q'_i}, \quad (47)$$

$$L_{\Theta_{ij} u_k} \rightarrow L_{\psi u_k} = \nabla_{r_k} \psi(\mathbf{r}, \mathbf{Q}) + \nabla_{Q_k} \psi(\mathbf{r}, \mathbf{Q}) Q_m \nabla_{r_m}. \quad (48)$$

As a consequence of the degeneracy requirement (2), the bulk pressure p is again given by Eq. (24) and the osmotic pressure is [29]

$$\Pi = n_p(2k_B T - H\Theta). \quad (49)$$

As far as the irreversible dynamics is concerned, i.e., the operator M , we note that the relaxation or diffusion of the distribution function is not coupled to the irreversible behavior of any other of the variables in Eq. (45). Therefore, we can exclusively concentrate the discussion on the element $M_{\psi\psi}$, the other elements in the ψ rows and columns being zero. Due to the fact that the irreversible dynamics in Eq. (38) is given by $M_{\psi\psi} \delta S / \delta \psi$ and considering the form of the functional derivative (46), the most natural choice for a positive semidefinite element $M_{\psi\psi}$ is

$$M_{\psi\psi} = -\nabla_{Q_m} 2T \psi \bar{D}_{mn} \nabla_{Q_n} \quad (50)$$

with a symmetric, positive semidefinite diffusion tensor \bar{D}_{ij} . This choice is inspired by the symmetry requirement of M and by the need for second-order derivatives in the dynamic equation. The goal of formulating a diffusion equation for a linear stochastic process requires all elements \bar{D}_{ij} to be independent of \mathbf{Q} due to the specific form of $\delta S / \delta \psi$. The matrix M in Eq. (27) with the lower right corner replaced by $M_{\psi\psi}$ in Eq. (50) satisfies all requirements of the framework.

As a result of the above building blocks, the diffusion equation takes form (38), in agreement with the construction of a linear stochastic process, under the constraint $A_{ij} = D_{ij}$. By virtue of Eqs. (39) and (40), this results in a condition for gauge parameters G_{ij} ,

$$\langle (\partial_{Q_j} R_{ik}) Q_k \rangle_{\psi(t)} + k_B T G_{ij} = \frac{H}{2} (G_{ik} \Theta_{kj} + \Theta_{ik} G_{jk}). \quad (51)$$

It can be shown that due to the index structure, there is no solution G_{ij} to the thermodynamically imposed condition (51) for general flow situations. Note that for the preaveraging and self-consistent averaging method, for which the first term on the left side of Eq. (51) vanishes, we would find a solution, namely, $G_{ij}=0$. Thus, although the Gaussian approximation is valuable in terms of the second-moment equation (35), there is no underlying stochastic process \mathbf{Q} , from the thermodynamic perspective. Interesting enough, the very same mean-field approximation is also in conflict with the Green-Kubo relation. This connection shall be elaborated in more detail below in the context of linear response theory.

C. Relation to linear response theory for mean-field approximations

We now illustrate why ansatz (50) and the thermodynamically imposed constraint (51) are in harmony with the fluctuation-dissipation theorem of the first kind for the zero-shear rate viscosity. Consider a diffusion equation of the form

$$\partial_t \psi = (\mathcal{L} + \mathcal{L}_p) \psi, \quad (52)$$

where \mathcal{L}_p denotes the perturbative influence of an externally imposed flow field and, per definition, depends *explicitly* on the deformation rate. If we, furthermore, allow that both operators \mathcal{L} and \mathcal{L}_p depend by means of mean-field contributions on the distribution function ψ , they both possess an *implicit* dependence on the deformation rate in addition. Thus, the zeroth- and first-order contributions in the deformation rate to Eq. (52) read

$$0 = \partial_t \psi^{[0]} = \mathcal{L}^{[0]} \psi^{[0]}, \quad (53)$$

$$\partial_t \psi^{[1]} = \mathcal{L}^{[0]} \psi^{[1]} + (\mathcal{L}^{[1]} + \mathcal{L}_p^{[1]}) \psi^{[0]}, \quad (54)$$

where we have used $\mathcal{L}_p^{[0]} = 0$. The first-order operator $\mathcal{L}^{[1]}$, which is purely due to the dependence on the distribution function ψ , is of particular interest. In Ref. [30], where the effect of the mean-field approximation on linear response theory and fluctuation-dissipation theorems is discussed, it was shown that this specific term either leads to a modified interpretation or even to a failure of the usual fluctuation-dissipation theorem.

Let us now examine this situation for the above thermodynamically formulated distribution function model, namely, employing the thermodynamically imposed constraint $A_{ij} = D_{ij}$ (51). In pure homogeneous shear flow,

$$\boldsymbol{\kappa} = \begin{pmatrix} 0 & \dot{\gamma} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (55)$$

the operators $\mathcal{L}^{[0]}$, $\mathcal{L}^{[1]}$ and $\mathcal{L}_p^{[1]}$ corresponding to diffusion equation resulting from the building blocks E [Eq. (18)], S [Eq. (46)], L [Eqs. (19)–(21), (47), and (48)] and M [Eq. (50)] are given by

$$\mathcal{L}^{[0]} = \nabla_{Q_i} 2k_B T \bar{D}_{ij}^{[0]} \nabla_{Q_j} + \nabla_{Q_i} 2\bar{D}_{ij}^{[0]} H Q_j, \quad (56)$$

$$\mathcal{L}^{[1]} = \nabla_{Q_i} 2k_B T \bar{D}_{ij}^{[1]} \nabla_{Q_j} + \nabla_{Q_i} 2\bar{D}_{ij}^{[1]} H Q_j, \quad (57)$$

$$\mathcal{L}_p^{[1]} = -\nabla_{Q_i} \kappa_{ij} Q_j, \quad (58)$$

if the perturbation parameter is the infinitesimally small shear rate $\dot{\gamma}$. Because $\mathcal{L}^{[0]} \psi^{[0]} = 0$ per definition, we find immediately as a direct consequence of $A_{ij} = D_{ij}$ that

$\mathcal{L}^{[1]} \psi^{[0]} = 0$, which is exactly the arguable term. Hence, the thermodynamic treatment automatically does not conflict with the Green-Kubo relation. This again highlights the importance of the thermodynamically imposed condition $A_{ij} = D_{ij}$ (51) for Eq. (38), which does not hold for the gauge $G_{ij} = 0$, the latter therefore violating the Green-Kubo relation as shown in Eq. (43). For completeness, we wish to mention that $A_{ij} = D_{ij}$ (51) can be enforced up to first order by an appropriate choice for $G_{ij}^{[0]}$, resulting in $\mathcal{L}^{[1]} \psi^{[0]} = 0$ and in fulfilling the Green-Kubo relation. However, such a “solution” shall not be considered, since it cannot be extended into the nonlinear flow regime, and thereby prohibits the construction of a stochastic process defined in all flow regimes.

D. GENERIC second-moment formulation with fluctuations

The above discussion has shown clearly that the construction of a stochastic process \mathbf{Q}_t underlying the Gaussian approximation is dubious. However, in view of the Green-Kubo relation (42) between the average stress and its fluctuations, we lift the model to a different level by focusing on the second moment, i.e., on the stress tensor according to Eq. (49), as primary dynamic variable with fluctuations, instead of \mathbf{Q}_t . To formulate the according stochastic differential equation for the second moment, we use the GENERIC with fluctuations [8,31]. As shown in the following, this model indeed does satisfy the Green-Kubo relation (42).

The set of variables being the hydrodynamic variables and the second moment, i.e., Eq. (9), the purely entropic origin of the Hookean spring force again leads to the total energy (10), whereas the entropy is given by (see also p. 6648 in Ref. [9])

$$S = \int \left(s(\rho, \epsilon) + \frac{n_p k_B}{2} \ln \left[\det \frac{H}{k_B T} \boldsymbol{\Theta} \right] - \frac{n_p H}{2T} \text{tr} \boldsymbol{\Theta} \right) d^3 r. \quad (59)$$

Similar to example 1, the functional derivatives are given by Eq. (18) but with a configuration independent spring constant H this time. This being the only difference allows one to refer to Eqs. (19)–(25) as a valid Poisson operator for the reversible dynamics of the present example with the osmotic pressure tensor (26) having a configuration independent spring constant. The friction matrix M for the irreversible dynamics is again of form (27). In view of the second-moment equation (35), the fourth-rank tensor S_{ijkl} in Eq. (27) is given by Eq. (36), which inherits the symmetry and positive semidefiniteness from \hat{R}_{ij} . This completes the GENERIC description of the deterministic second-moment equation (35).

In order to include fluctuations consistently, we consider the GENERIC with fluctuations [8,31], which in general terms is given by the Itô stochastic differential equation [21,27]

$$dx = L \frac{\delta E}{\delta x} dt + M \frac{\delta S}{\delta x} dt + k_B \frac{\delta M}{\delta x} dt + B dW_t, \quad (60)$$

where B is a solution of the equation

$$BB^T = 2k_B M \quad (61)$$

and W_t is a multicomponent Wiener process. Expression (61) for B may be regarded as the fluctuation-dissipation theorem of the second kind [26].

For the set of variables (9) and according to Eq. (60) with the building blocks E [Eq. (10)], S [Eq. (59)], L [Eqs. (19)–(25), and (26)] with constant spring constant H , and M [Eqs. (27) and (36)], the stochastic differential equation for the second moment is then given by

$$d\Theta_{ij} = \left[-v_k \partial_k \Theta_{ij} + \kappa_{im} \Theta_{jm} + \kappa_{jm} \Theta_{im} + S_{ijkl} \left(\frac{kT}{2} \Theta_{kl}^{-1} - \frac{H}{2} \delta_{kl} \right) + k_B \left(\frac{\partial S_{ijkl}}{\partial \Theta_{kl}} \right) \right] dt + \tilde{B}_{ijkl} dW_{t,kl}, \quad (62)$$

where the contributions in the second line are due to the added fluctuations. Due to the specific form of the M matrix (27), one can find \tilde{B}_{ijkl} such that

$$\tilde{B}_{ijmn} \tilde{B}_{klmn} = \frac{2k_B T}{n_p} S_{ijkl}. \quad (63)$$

We now consider small perturbations of the second moment Θ_{ij} around its equilibrium value $(k_B T/H) \delta_{ij}$, due to flow and/or due to thermal fluctuations. In order to respect the GENERIC structure, and in particular relations (61) and (63), it is essential to expand the building blocks rather than directly the contributions in the second-moment equation. Denoting the deviation from the equilibrium value by

$$\varepsilon_{ij} \equiv \Theta_{ij} - \frac{k_B T}{H} \delta_{ij}, \quad (64)$$

one finds that for $\partial_t \varepsilon_{ij}$ only the zeroth-order contribution of S_{ijkl} , $S_{ijkl}^{(0)}$, is relevant, *not only* in the last term in the first line of Eq. (62) *but also* for both terms in the second line. In this way, the first term in the second line of Eq. (62) vanishes and the difference among the Itô, Stratonovich, and kinetic interpretations of stochastic calculus [21,32] is erased. For small velocity perturbations or thermal fluctuations, the perturbation of the second moment is, therefore, given by

$$d\varepsilon_{ij} = \left[\frac{k_B T}{H} (\kappa_{ij} + \kappa_{ji}) - \frac{H^2}{2k_B T} S_{ijkl}^{(0)} \varepsilon_{kl} \right] dt + \tilde{B}_{ijkl}^{(0)} dW_{t,kl}, \quad (65)$$

where $\tilde{B}_{ijkl}^{(0)}$ is related to $S_{ijkl}^{(0)}$ through the Choleski decomposition (63). Equation (65) allows us to draw two conclusions. First, the average of the first-order perturbation $\langle \varepsilon_{ij} \rangle$ is not affected by the fluctuations. Thus, the zero-shear rate viscosity determined from linear response theory, i.e., η_0^{LR} computed previously, is not changed. The second conclusion is related to the Green-Kubo relation for the zero-shear rate

viscosity, η_0^{GK} . Since one can show that $S_{ijkl}^{(0)}$ is nonzero only if the indices are pairwise identical, the equilibrium correlation function of the shear component of the stress tensor can be computed. After a straightforward calculation for the Oseen-Burgers tensor, one finds

$$\eta_0^{\text{GK}} = \frac{k_B T \zeta / H}{1 - \frac{7}{10} \sqrt{2} h^*} = \eta_0^{\text{LR}}, \quad (66)$$

i.e., the fluctuation-dissipation theorem for the zero-shear rate viscosity is respected. It must be emphasized that taking proper care of the connection between the terms in Eq. (62) and the building block M was essential.

To summarize the discussion on the Gaussian approximation, we have shown that no diffusion equation in accordance with the original Gaussian approximation can be constructed which both respects the Green-Kubo relation for the zero-shear rate viscosity and is defined also in nonlinear flow regimes. However, considering the second moment as dynamic variable with fluctuations resulted in a thermodynamically admissible model along the guidelines of fluctuating GENERIC, which respects the Green-Kubo relation and is defined for all flows.

V. CONCLUSIONS

The introduction of mean-field approximations into dynamic equations has been examined in two examples from the perspective of nonequilibrium thermodynamics, employing the GENERIC formalism.

In the first example, de Gennes's second-moment tensor model to study the effect of chain deformations in fast flows has been studied. This model is here considered to be self-contained, rather than an approximate version of a diffusion equation, which demands the verification of the thermodynamic admissibility of de Gennes's model as such. It has been found that this model can be formulated in the GENERIC framework and is in that respect considered thermodynamically admissible, as well as the associated coil-stretch transition.

The second example was concerned with a Gaussian approximation, defined on the second-moment level, for hydrodynamically interacting Hookean dumbbells. According to nonequilibrium thermodynamics, there is no diffusion equation for the underlying connector vector distribution which, first, respects the Green-Kubo relation and, second, is defined also in nonlinear flow regimes. The capability of the technique to reveal this defect of the approximation constitutes a major result. Furthermore, specifically the GENERIC framework offers means to study fluctuations on the second moment. Thereby, a model was developed for the second moment as primary dynamic variable, which respects the Green-Kubo relation for the shear stress and is defined also in nonlinear flows.

As a result, it emerges that using nonequilibrium thermodynamics techniques is beneficial for formulating models with mean-field approximations, and prevents from inconsis-

tent or defective approximations (see example 2). This is achieved through modifying and approximating the building blocks of the formalism employed, rather than the resulting dynamic equations. We should mention that, although we have here used the GENERIC framework, these general re-

marks also hold for other formalisms such as the single-generator bracket formalism [7]. However, the method employed must allow for nonlinear models, as was demonstrated in example 2 when aiming at a model defined for arbitrary flow conditions.

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